VAPOR PRESSURE OF OXIDES OF LITHIUM,

BERYLLIUM, BORON, SILICON AND LEAD

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In connection with the development of vacuum metallur-
gy and vacuum technology as well as a number of other indus-
trial fields, the behavior of metallic oxides at high tempe-
ratures under vacuum is of great interest, in particular the
oxides of lithium, beryllium, boron, silicon and lead.
Valuable data on the thermodynamic properties of the-
se substances can be obtained from determinations of vapor
pressure equilibrated with corresponding condensation phases.
A number of works treating the vapor pressure of li-
thium, beryllium, boron, silicon and lead oxides (1-9) are
described in the literature. However, the published data is
barely consistent; in addition, in a whole group of cases,
methodical errors have been found which are due to an insuf-
ficient account having been taken of characteristics of the
vaporization processes of the oxides. The extremely high re-
action capacity of the investigated oxides causes signifi-
cant difficulties in working with these substances.
The experimental determination of the vapor pressure
of lithium, beryllium, boron, silicon, and lead oxides gives
rise to two possible ba.ic types of secondary reactions.
In the first place, there is the reaction between the
oxides and the components of the air or residual gas, and in
the second place, the reaction between the oxides and the ma-
terials of the containers from which the vaporization takes
place.
In reactions of the first type, stable hydroxides or
carbonates are formed in the vapor phase, the volatility of
which can significantly exceed the volatility of the corres-
ponding oxides. The result of the reaction of the second type
is that the oxides can either be reduced by the metallic con-
tainers or they can form solutions with the ceramics used in
the preparation of the various parts of the containers.
In the vaporization of oxides, since both types of se-
condary reactions lead to the formation of various volatile

compounds, the experimental results can be distorted. Therefore, in the determination of the vapor pressure of oxides particular attention should be paid to conducting the experiments under conditions which exclude any interaction of the oxides.

In the present work the vapor pressure, equilibrated with heavy oxides of lithium, beryllium, silicon, lead, and fused boron oxide, was measured by an integral variant of the effusion method /10/. For the determination of vapor pressure values of beryllium, silicon and lead oxides, the rate of vaporization of these substances from an open surface in vacuum was also measured.

The work was carried out with specially purified oxides. The impurity content, determined by spectral and other micro-chemical analytical methods, was shown to be: oxide of beryllium - 0.7 percent, oxide of lithium - 0.25 percent, oxide of lead (lead monoxide) - 0.05 percent, boron oxide - 0.01 percent, and silicon dioxide (alpha-tridymite) - 0.10 percent.

To determine crystalline modification forms, X-ray analysis was carried out. All the analytical operations and the loading of the containers with the preparations were carried out in a dry chamber in an atmosphere of purified argon.

In order to eliminate the reaction between the oxides and the water vapor or other components of residual gases and air, the vaporization experiments were either conducted in an installation, whose construction made it possible to conduct the whole series of experiments without breaking the high vacuum, or before each exposure, the substance was subjected to an additional baking in vacuum. For the preparation of containers, appropriate materials were chosen so as to eliminate the reaction of the second type.

The control as to the degree and character of interaction between the oxides and the materials of the containers was accomplished by means of chemical and X-ray analyses of the residual substance in the container, the condensate and surface layers of the internal parts of the effusion chambers and by both methods used on the samples.

As a result of the experimentation, it was established that for oxides of lithium, containers of the following metals would be most useful: nickel and platinum containers, for the oxides of silicon and boron - molybdenum or tantalum containers, for oxides of beryllium - tungsten or ceramic containers; ceramics was used also in experiments with lead oxide.

The construction of the containers used was odrinary and was determined by the experimental conditions. Heating was carried out with high frequency currents or by means of

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spiral-heated ovens, during which, in the case of spiral heaters, the temperature was regulated and maintained constant during the experiment with a precision of up to $\pm 0.5°$. With induction heating the precision of temperature regulation was somewhat lower. The temperature was measured with a platinum --- platinum-rhodium thermocouple or with an optical pyrometer measuring the temperature of the substanc's surface through a viewing window provided with a protective sliding plate. The thermocouple and the pyrometer were calibrated directly in the apparatus according to the melting point of silver, gold, platinum, etc., or according to the vapor pressure of potassium chloride or silver.

The amount of matter, vaporized from the effusion chamber or from the surface of the samples in vacuum was determined both as the weight of the collected condensate and the loss in weight of the container from which the oxides were vaporized. According to the amount of vaporized matter, the values of the vapor pressure of the appropriate substances were calculated. The assumption was made that all the oxides have condensation coefficients in the vicinity of unity and vaporize without change of molecular composition.

The proximity of the condensation coefficients to unity was confirmed in a series of experiments. Thus the condensation coefficients of beryllium and lead oxides were evaluated by comparing their vapor pressure values obtained by the Knudsen method and the vaporization method from an exposed surface in vacuum. The condensation coefficients of lithium, boron and silicon oxides were determined by measuring their vapor pressures by the Knudsen method using effusion apertures of various areas. For an additional evaluation of the corresponding coefficients of beryllium, boron and lead oxides, a method was developed by us for determining the relationship between the measured vapor pressure and time under conditions of effusion experiments.

The rapid saturation by the vapors of the chambers' volume confirmed the assumption that the value of the condensation coefficients of these substances was close to unity.

The processing of experimental data on the oxides studied, by the method of least squares, yielded the following equations characterizing the relationship between vapor pressure values and time:

| | | |
|---|---|---|
| lithium oxide | $\lg Pat = 7.48 - 18400/T$ | $(1383 - 1506°K)$ |
| beryllium oxide | $\lg Pat = 8.16 - 33200/T$ | $(2103 - 2573°K)$ |
| boric oxide | $\lg Pat = 6.56 - 16800/T$ | $(1299 - 1515°K)$ |

silicon dioxide
alpha-tridymite       $\lg P_{at} = 3.27 - 16600/T$   $(1601 - 1754^{o}K)$

Lead monoxide
massicot             $\lg P_{at} = 8.70 - 13900/T$   $( 887 - 1151^{o}K)$

CONCLUSIONS: 1. The vapor pressure of lithium, beryllium, boron, silicon and lead oxides was mwasured by the effusion method.

2. The vapor pressure of beryllium, silicon and lead oxides was measured by the vaporization method from an exposed surface in vacuum.

3. It was shown that the condensation coefficients of the investigated oxides were close to unity.

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